

Taking the Salt Out of the Sea

WATER is a precious natural resource and one of the basic building blocks of life. Yet, according to UNICEF, nearly one in six people worldwide lacks access to clean drinking water. In some areas, water scarcity has resulted in conflict between neighboring states. As demand for this resource continues to increase globally, finding ways to make more of Earth's water—97 percent of which is seawater—fit for human consumption will be of great importance in creating an adequate clean water supply for the billions of people worldwide.

A novel R&D Award—winning membrane technology developed by Lawrence Livermore in partnership with Porifera, Inc., in Hayward, California, and with early support from Livermore's Laboratory Directed Research and Development Program, could lead to more cost-effective filtration processes for water desalination and reclamation than are available today. The highly permeable, chemically inert membranes are composed of carbon nanotubes (CNTs), which are hollow, seamless cylinders. Extremely smooth interior walls allow liquids and gases to rapidly flow through CNTs, while rejecting larger molecules.

Because of a CNT membrane's sophisticated structure and material properties, solutes such as salt and other ionic compounds can be filtered out of seawater or brackish water using substantially less energy than is needed to achieve similar results with conventional polymer-based membranes. Although the high energy costs and relatively low efficiencies of standard water filtration

processes have hindered development of large-scale desalination facilities in the past, CNT membranes could help make such facilities a widespread reality.

Molecules Go with the Flow

Billions of carbon nanotubes, each one about 50,000 times thinner than a human hair, are grown on a single silicon substrate using chemical vapor deposition. (See *S&TR*, January/February 2007, pp. 19–20.) The space between this "forest" of nanotubes is then filled with a matrix material such as silicon nitride to create the membrane. Excess material is removed from either end, and the top and bottom of the nanotubes are reopened using a reactive ion-etching process.

"The primary advantage to CNT membranes is that water flows through them at a rate 1,000 times faster than through the polymer-based membranes typically used in water filtration equipment," says former Livermore scientist Jason Holt. This fast transport is made possible because of the unique properties of a CNT's inner surface, which is atomically smooth, hydrophobic, and nonpolar with a uniform distribution of electrons. As a result, water molecules, which are polar in nature, bond to each other instead of to the CNT walls, enabling them to move together rapidly in a continuous chain. "This frictionless flow," says Olgica Bakajin, another former Livermore scientist who coled the

research, "could result in a more than 20-percent reduction in energy consumption for seawater desalination and a more than 80-percent reduction for brackish water desalination."

Nanotubes Perform Well under Pressure

Reverse osmosis is a popular technique for liquid desalination. In this process, pressure is applied to a saline solution, and the liquid is pushed through a semipermeable membrane that blocks the passage of sodium chloride or other dissolved solids. Thus, the water that passes through to the other side of the membrane is purified. Because of the laws of thermodynamics, enough pressure must be applied to prevent the purified water from passing back through the membrane into the saline solution. "We must overcome the difference between the osmotic pressure of the seawater and the pure water to separate the water from the salt," says former Livermore scientist Aleksandr Noy, who also coled the development effort.

Polymer-based membranes are less permeable than those made from CNTs and thus need more pressure to obtain the desired flow rate. Unfortunately, water filtration equipment consumes more energy to produce higher pressures, which substantially increases operational costs. To increase flow rate without increasing operational pressure, manufacturers build conventional membranes as thinly as possible. However, thinner membranes are more susceptible to developing defects, such as pinholes, that reduce the membrane's efficiency. In addition, under pressure, the membrane pores constrict, further reducing the already limited flow.

In contrast, CNT membranes have intrinsically higher permeability than conventional membranes, so they can be made thicker without sacrificing flow rate. This thicker "skin" reduces the likelihood of pinhole defects, and the membranes' overall composition makes them immune to deleterious compaction effects.

Versatile Membranes

Livermore licensed the technology to Porifera, Inc., in 2009, and the product is undergoing commercial development and testing. Its price is expected to be approximately \$20 per square meter, which is comparable to the price of existing polymer-based membranes. And CNT assemblies can be built to the specifications required for replacing membrane cartridges within existing equipment, eliminating the potential for additional infrastructure costs to support the technology.

Another benefit of CNT membranes is that they can be customized for a variety of applications. At Livermore, they are being applied to several areas of research. "We're using this technology as part of an effort to develop breathable fabrics for protective clothing," says Livermore scientist Francesco Fornasiero. The fast transport capabilities of CNT membranes allow water vapor to escape through the material, unlike most protective fabrics that keep moisture in. People wearing the material can stay cooler, longer. "These fabrics would help prevent heat stress in people such as soldiers and firefighters working in hazardous, high-temperature environments," he says.

CNT membranes are also playing a role in national security and carbon sequestration research. "They could potentially overcome the limitations of gas separation membrane technologies as well as current carbon dioxide separation

> processes," says Sangil Kim, also formerly of Livermore. Ideally, CNT membranes could be used to separate carbon dioxide from the flue gas generated by industrial facilities such as coal-fired power plants. From helping to increase the world's clean water supply

> > to reducing carbon emissions, CNT membranes may become essential to managing natural resources for future generations.

—Caryn Meissner

Key Words: carbon nanotube (CNT) membrane, desalination, filtration, R&D 100 Award, reclamation, reverse osmosis.

For further information contact Francesco Fornasiero (925) 422-0089 (fornasiero1@llnl.gov).

